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1 **Silica-Modifying Chemical Admixtures for Directed Zeolitization of Metakaolin-based** 2 **Alkali-Activated Materials**

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7

8 **Abstract**

9 The effect of using trimethyladamantyl-ammonium hydroxide (TMAAOH) as a silica-modifying admixture
10 to induce early-age mineralization during alkali-activation of metakaolin was investigated and reported
11 herein. In all material formulations, the use of TMAAOH induced early-age mineralization, increased
12 mixture stiffening in the fresh state, and lowered total heat of reaction. In activating solutions with silica
13 moduli above unity ($M_s > 1.0$), mineralogy results demonstrate that TMAAOH induces the nucleation and
14 growth of metastable zeolitic phases, which correlated with increased permeability and increased plastic
15 shrinkage of the paste. When TMAAOH was added to activating solutions with silica moduli near unity
16 ($M_s \sim 1.0$), the controlled formation of crystalline, silica-rich faujasite was observed, which correlated with
17 reduced permeability and lower plastic shrinkage. Together, these results demonstrate for the first time that
18 silica-templating agents such as TMAAOH can be exploited in the design of new chemical admixtures that
19 directly influence the dynamics of zeolitization in alkali-activated materials.
20

21 **Keywords:** zeolites; mineralization; alkali-activated cements; rheology.
22

23 **1.0 Introduction**

24 Alkali-activated materials (AAMs) are a class of aluminosilicate cementitious materials produced by
25 mixing aluminosilicate precursor powders (*e.g.*, fly ash, slag, metakaolin) with alkaline activating solutions
26 (*e.g.*, NaOH, KOH). In general, AAMs can be classified by the cementitious binder that composes them,

27 which varies depending on the calcium content available in the precursor [1]. Low-calcium AAM binders,
28 which contain significantly lower calcium than conventional Portland cement (PC) [2–4], predominantly
29 consist of a sodium-stabilized aluminosilicate hydrate framework (*i.e.*, N-A-S-H), although other alkalis
30 can be used as charge-balancing cations. The short-range structure of NASH as a 3D aluminosilicate
31 network has been recently studied and reported in [3].

32 The distinct chemistry of low-calcium AAMs has permitted their versatile utilization in a wide range
33 of applications from construction [5], water filtration [6], soil stabilization [2], and nuclear waste
34 containment [7], among others [8–10]. In the construction industry, AAMs offer a promising alternative to
35 PC materials in certain applications due to lower cradle-to-gate CO₂ emissions, comparable mechanical
36 properties, and, in some cases, improved durability [11,12].

37 ***1.1 Mineralogical Composition of AAMs***

38 Understanding and controlling zeolite formation is a critical factor in developing durable microstructures
39 in low-calcium AAMs. The combination of low-calcium aluminosilicate precursors (*e.g.*, metakaolin,
40 clays) and both high-temperature and high-humidity curing conditions often induces the formation of
41 zeolites [13]. The type, amount, and thermodynamic stability of zeolites that form can vary widely [14,15].
42 Zeolites are well known to affect the physical, mechanical, and durability properties of AAMs [15].
43 Zeolitization in AAMs has been linked with reduced porosity [13], potential chloride binding [16,17],
44 mitigation of acid degradation [18], decreased efflorescence due to reduced sodium leaching [19], and
45 heavy-metal and radioisotope immobilization [8,20,21].

46 Zeolite formation in AAMs is identical to the sol-gel processes utilized to create synthetic zeolites.
47 Both processes involve Si, Al, and alkali metals (*e.g.*, Na⁺, K⁺). Gevaudan *et al.* identified that both sodium-
48 to-alumina ratio (Na:Al) and silica availability (*i.e.*, liquid vs. solid silica additions), along with
49 environmental conditions during curing (*i.e.*, temperature, relative humidity) are critical factors that affect
50 the formation of crystalline zeolite phases [13]. More specifically, high silica availability and high Na:Al
51 ratios can lead to the early-age formation of faujasite zeolites in metakaolin-based AAM pastes [13]. Other

52 studies have confirmed that zeolite formation is favored at high alkali (*i.e.*, Na:Al > 1) and low silicon
53 contents (*i.e.*, Si:Al ≤ 4), and when cured at elevated temperature and humidity [22,23].

54 In synthetic chemistry, zeolization can be precision-tailored using organic cationic templating
55 agents (*e.g.*, quaternary ammonium compounds) [24–26]. Briefly, templating agents physicochemically
56 interact with dissolved silica species and induce the nucleation and growth of zeolites in a templating
57 fashion. The resulting zeolite mineralogy and metastability depends precisely on how oxide tetrahedra are
58 structured into specific geometric arrangements [24].

59 These arrangements are primarily driven by the host-guest interactions between the organic cation
60 and the silicate species that surround it. These interactions are influenced by the size and shape of the
61 organic molecule, its hydrophobicity (or hydrophilicity), hydrothermal stability, and the rigidity or
62 flexibility of its molecular bonds [24]. Diverse in their functionality, templating agents guide the
63 stabilization of the aluminosilicate framework by initiating the formation—and ultimately dictating—the
64 crystal size, morphology, and chemical composition of zeolites. A thorough review of the structure-
65 directing agent phenomena can be found in [24].

66 **1.2 Scope**

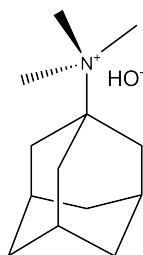
67 The purpose of this study was to use an organic templating agent, namely trimethyladamantyl-ammonium
68 hydroxide (TMAAOH), as a structure-directing chemical admixture for the express purpose of inducing
69 early-age zeolitization in low-calcium AAMs. In addition to zeolitization, the associated effects on reaction
70 kinetics, fresh-state behavior, and bulk material properties of AAM pastes were investigated and reported
71 herein.

73 **2.0 Materials and Methods**

74 **2.1 Materials**

75 Metakaolin (MK) (MetaMax) was supplied by BASF (Georgia, USA). The chemical composition of the
76 MK used in this study was previously reported by the authors in [13], and its X-ray diffractogram can be
77 found in **Figure S1**. Reagent-grade sodium hydroxide (NaOH) pellets with >97% chemical purity and

78 sodium silicate (NaSi) $M_s=2.5$ ($\text{SiO}_2 = 27 \text{ wt}\%$, $\text{Na}_2\text{O} = 11 \text{ wt}\%$, $\text{H}_2\text{O} = 62 \text{ wt}\%$), were obtained from
79 Sigma-Aldrich (St. Louis, MO, USA). TMAAOH was obtained from SACHEM (Austin, TX, USA). **Figure**
80 **1** shows the structure of TMAAOH. Lastly, ethanol (200 proof) was obtained from Fisher Scientific
81 (Hampton, NH, USA).



82
83 **Figure 1:** Chemical structure of TMAAOH.
84

85 **2.2 Experimental Methods**

86 **2.2.1 Mixture Design & Sample Preparation**

87 Twelve MK-based AAM paste mixtures were prepared by varying the Si:Al and Na:Al ratios according to
88 the mixture design parameters listed in **Table 1**. A liquid-to-solid ratio of 2.0 was held constant across all
89 samples. A TMAAOH:SiO₂ ratio of 0.02 was selected based on previous research reported in zeolite
90 synthesis literature [27–30].

91 During preparation, the activating solutions were prepared by slowly dissolving the NaOH pellets
92 in deionized (DI) water before adding sodium silicate. After having equilibrated for 24 hours at ambient
93 conditions, the activating solution was manually mixed with MK then together with TMAAOH. The paste
94 was then mechanically stirred for 3 minutes.

95 While some freshly mixed materials were tested for rheological (section 2.2.2) and calorimetric
96 (section 2.2.3) behaviors, for all subsequent testing, the remaining materials were cast into 12x24mm HDPE
97 cylindrical molds and cured under ambient humidity and pressure at 80 °C. After 7 days' curing,
98 characterization experiments, including X-ray diffraction (XRD), plastic shrinkage, and permeable
99 porosity, were conducted. Additional XRD patterns were also collected after 3 days of curing.

100

101 **Table 1:** Paste mixture formulations without and with TMAAOH addition. Silica modulus (Ms) is
 102 equivalent to the SiO₂/Na₂O molar ratio in the chemical activating solution. Si:Al, Na:Al,
 103 TMAAOH:SiO₂ refer to the molar ratios of the final mixture.

104

Mixture	MK (g)	NaSi (mL)	NaOH (g)	Na ₂ O/100g of Binder	Si:Al	Na:Al	Ms	TMAAOH:SiO ₂	L/S
1	30	25	5	25.9	1.57	0.92	1.26	0	2.0
2								0.020	
3			10	38.8		1.37	0.84	0	
4								0.020	
5			15	51.7		1.84	0.63	0	
6								0.020	
7		45	5	36.1	2.03	1.28	1.62	0	
8								0.020	
9			10	49.0		1.74	1.19	0	
10								0.020	
11			15	61.9		2.21	0.94	0	
12								0.020	

105

106 2.2.2 Rheological Flow Curves

107 The rheological properties, namely yield stress and plastic viscosity, of MK-based AAM pastes, were
 108 determined with a MCR 301 rotational rheometer (Anton Paar, Graz, Austria). A 25 mm diameter stainless
 109 steel parallel plate geometry was used for all measurements, and the top plate was cross-hatched to
 110 minimize the influence of slip. The temperature was kept constant at 23 ± 0.1 °C, and the gap between the
 111 top and bottom plates was maintained at 1 mm. Prior to each test, approximately 700 μL of freshly mixed
 112 paste was transferred to the rheometer and subjected to pre-shearing at 50 s⁻¹ for 30 seconds, followed by a
 113 60 second rest period. The purpose of these pre-conditioning steps is to reduce the effects of shear history
 114 on the pastes and ensure reproducibility in testing [31]. The testing protocol consisted of linearly increasing
 115 the shear rate from 0 to 50 s⁻¹ in 10 discrete intervals over a period of 100 seconds. At each shear rate, the
 116 shear stress was measured, and these data were used to generate flow curves. The pastes were modeled as
 117 Bingham plastic fluids [32]. Each flow curve was used to calculate yield stress and plastic viscosity
 118 according to the Bingham equation:

119

$$\tau = \tau_0 + \mu\dot{\gamma} \quad (1)$$

120 where τ is the shear stress, τ_0 is the yield stress (Pa), μ is the plastic viscosity (Pa-s), and $\dot{\gamma}$ is the shear
121 rate (s^{-1}).

122 *2.2.3 Isothermal Conduction Calorimetry (ICC)*

123 A TAM Air 8-channel ICC (TA Instruments, New Castle, DE, USA) was used to evaluate the overall heat
124 output of the fresh paste mixes and to identify any zeolitization-induced heat (as described in [7]). The ICC
125 bath temperature was set to 80 °C and allowed to reach equilibrium over 3 days. Afterwards, an hour-long
126 gain validation was performed. Initial and final baselines were measured for 1 hour to minimize signal
127 noise. Around ten grams of freshly mixed paste was poured into glass ampules and placed in the calorimetry
128 chamber at 80 °C. Heat flow data were collected for seven days for all mixtures, and data were normalized
129 by the total mass.

130 *2.2.4 X-Ray Diffraction (XRD)*

131 Qualitative powder XRD analysis was performed with a Siemens D500 XRD (Bruker Corporation,
132 Billerica, MA, USA). Samples were soaked in ethanol for 24 hours after curing to halt time-dependent
133 chemical reactions. Subsequently, these were powdered and mixed with additional ethanol to form a slurry,
134 which was then pipetted onto a single crystal silicon no-background plate. All samples were analyzed from
135 5 to 65° 2 θ using Cu K α radiation with a step size of 0.02° and a 2s dwell time per step. XRD was performed
136 at 40kV and 30mA.

137 *2.2.5 Hardened-State Properties: Shrinkage, and Permeable Porosity*

138 Cylindrical specimens were removed from the curing chamber and demolded. Height and diameter
139 measurements were taken using calipers. Dimensional plastic shrinkage was calculated by subtracting the
140 diameter of the mold from the average diameter of the specimens after seven days of curing and determining
141 a percent difference. After physical measurements were taken, samples were dewatered using an ethanol
142 gradient to mitigate microcracking according to the following procedure. Samples were initially exposed
143 to a 10% ethanol and water solution for one hour. Every subsequent hour the ethanol percentage was
144 increased by 20%. Once samples were exposed to a 90% ethanol solution, they were exposed to a 100%
145 ethanol solution overnight [13]. After samples were fully saturated, they were massed (M_{sat}) and placed in

146 an oven at 60 °C for 24 hours [33,34]. Subsequently, the dry masses (M_d) of the samples were obtained.
147 Bulk density was determined by dividing M_d by the cylindrical volume (V_c) calculated from height and
148 diameter measurements for each sample. Lastly, permeable porosity was calculated as the difference
149 between M_{sat} and M_d normalized by the density of ethanol (0.789 g/cm³) and divided by the sample
150 cylindrical volume:

$$151 \quad Porosity = \frac{(M_{sat} - M_d)}{0.789 * V_c} \quad (2)$$

152

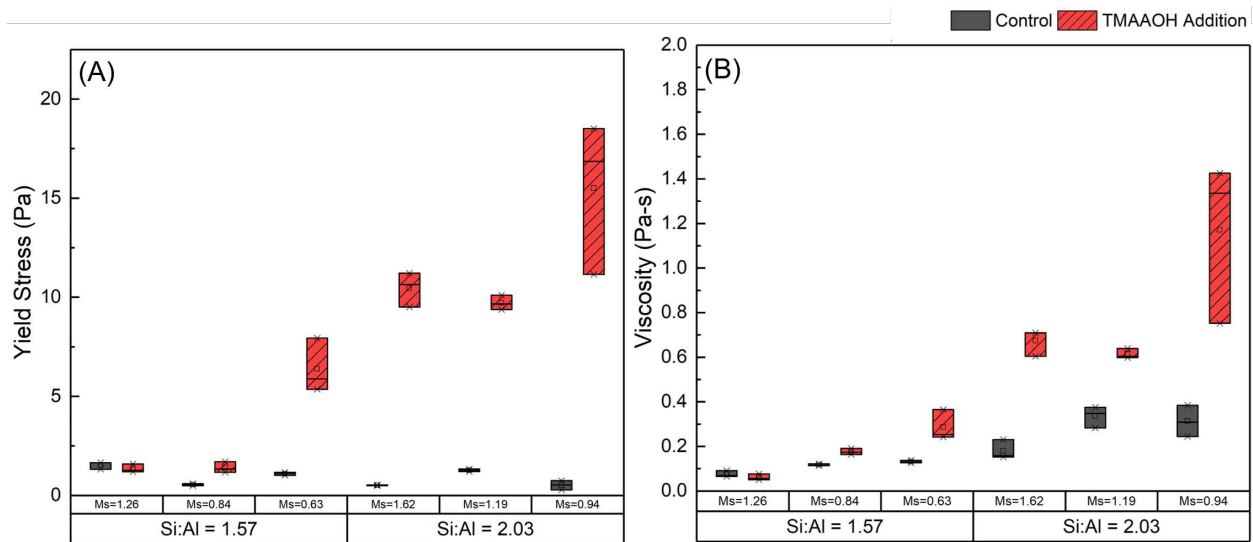
153 **3.0 Results and Analysis**

154 *3.1 Effect of TMAAOH on Rheological Properties*

155 The yield stress and plastic viscosity of each paste formulation are reported in **Figure 2**. Data
156 substantiate that the addition of TMAAOH increases both the yield stress and plastic viscosity of the pastes,
157 especially at low M_s and high Si/Al ratios. For example, in the mix with M_s of 0.63 and Si:Al ratio of 1.57,
158 addition of TMAAOH quadrupled the yield stress and doubled the viscosity. Such increases were even
159 more substantial as the Si/Al ratio increased to 2.03, regardless of the M_s value.

160 The rapid increase in both yield stress and viscosity suggests that TMAAOH interacts chemically
161 with the silicate species in the activating solutions. While a low- M_s value (*i.e.*, with high alkalinity) induces
162 rapid dissolution of the precursor and creates (alumino)silicate oligomers in solution [35–38], a high Si/Al
163 ratio also favors production of the oligomers [39,40]. In either case, these negatively-charged oligomers are
164 stabilized by the cationic sites of TMAAOH, the process known as the “templating effect” of organic
165 molecules. As a consequence, the stabilization of oligomers stiffens the mixture and yields discernible
166 increases in both the yield stress and viscosity of AAM pastes [41,42]. Thus, fresh state evidence indicates
167 that TMAAOH induces a templating—and stiffening—effect during alkali activation of MK as it does
168 during pure zeolite synthesis [43].

169 This study, in line with previous research, shows that TMAAOH-free MK pastes have yield stresses
170 < 2 Pa (**Figure 2**) [37,44]. The addition of TMAAOH increases the yield stress of all Si:Al=2.0 samples
171 from ~2 Pa to between 11-16 Pa (**Figure 2**).



172

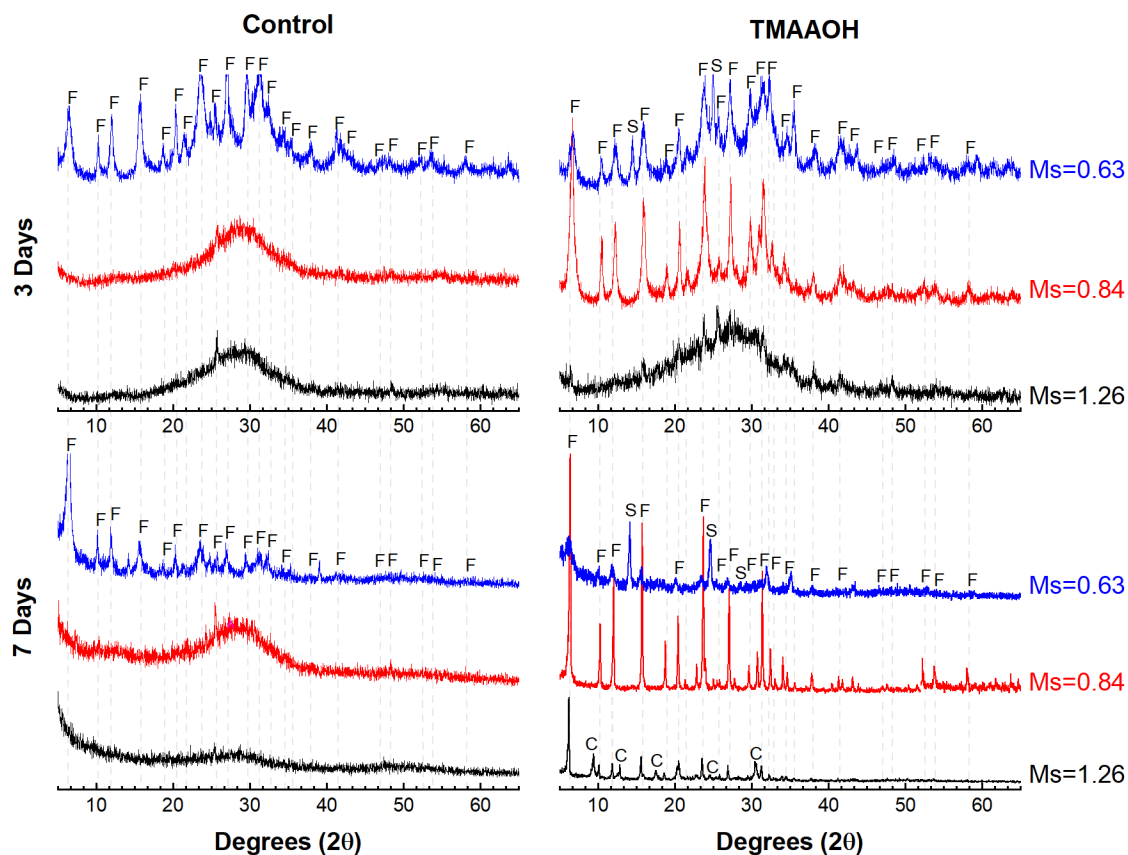
173 **Figure 2.** (a) Yield stress and (b) plastic viscosity of MK-based AAM pastes without and with TMAAOH
 174 addition. Error bars represent \pm one standard deviation ($n=3$).

175

176 3.2 Effect of TMAAOH on Mineralogy

177 **Figure 3** and **Figure 4** present the mineralogical data obtained from the AAMs at Si:Al ratios of 1.57 and
 178 2.03, respectively. It is evident that TMAAOH induced the formation of zeolites, such as faujasite (Si:Al =
 179 2.3), chabazite (Si:Al = 2.1), and sodalite (Si:Al = 1.0), in comparison to non-supplemented controls [45–
 180 47]. As explained previously, TMAAOH templates local silica oligomers during alkali activation, which
 181 mimics the direct *in situ* crystallization methods for pure zeolite synthesis [24,48]. In this methodology,
 182 aluminosilicate gels, produced during alkali-activation, precipitate onto the organic template, which
 183 facilitates zeolite nucleation and growth [30]. Mechanistically speaking, TMAAOH catalytically reduces
 184 the thermodynamic activation energy to nucleate zeolites [24,29,49–51].

185 The zeolite types induced by the TMAAOH were silicon-rich faujasite and chabazite or aluminum-
 186 rich sodalite. Silicon-rich chabazite has been previously identified in MK and fly ash activated materials,
 187 however, extended-time studies (>84 days) have revealed that this zeolite phase is largely metastable [52]
 188 and will thermodynamically transition to other more stable zeolitic phases over time. The identified zeolites
 189 were found to depend on the Ms value of the activating solution as discussed in the following section.



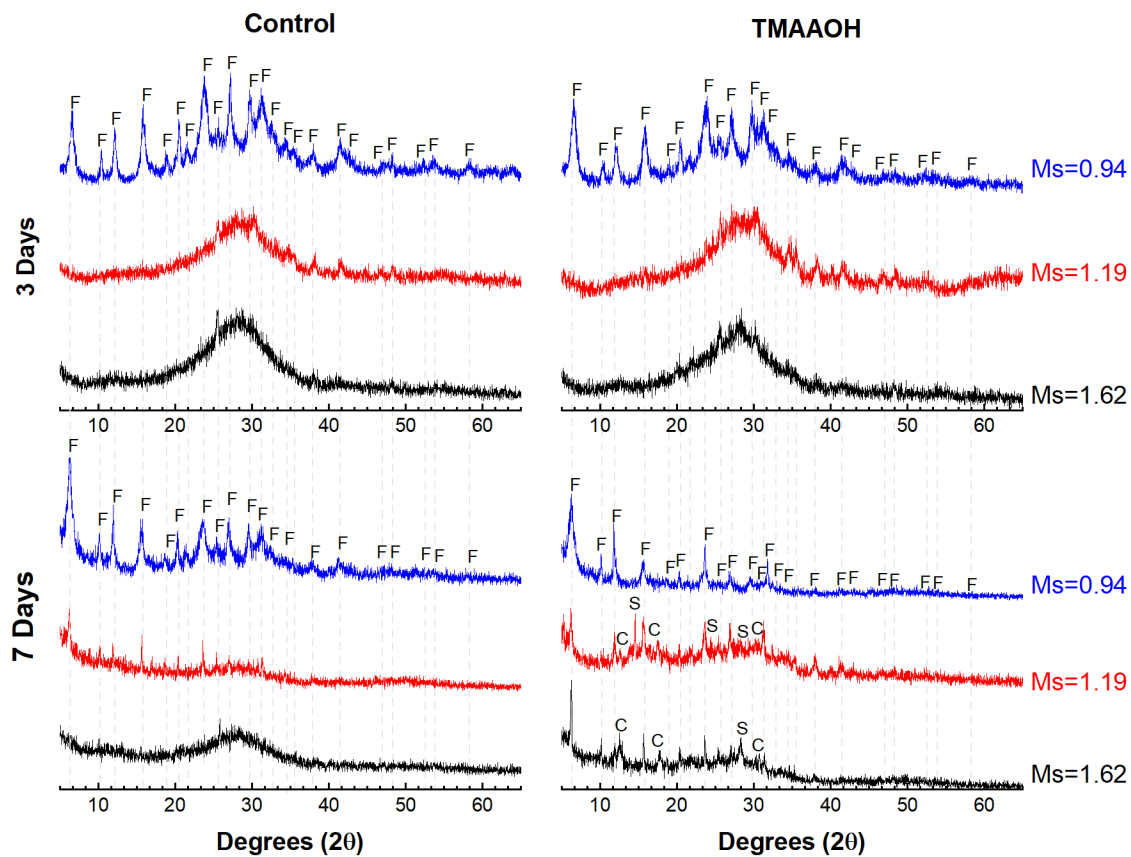
190
 191 **Figure 3.** X-Ray diffractograms of alkali-activated MK with Si:Al=1.57 at three (72 hours) and seven days
 192 (168 hours). C=Chabazite (*Si:Al* = 2.1, PDF 00-019-1178), F=faujasite (*Si:Al* = 2.3, PDF 00-012-0228),
 193 S = Sodalite Octahydrate (*Si:Al* = 1.0).

194
 195 In activating solutions with silica moduli (*Ms*) higher than unity (>1.0), zeolite nucleation induced
 196 by TMAAOH favored silicon-rich minerals (*i.e.*, chabazite and faujasite). From **Figure 3** and **Figure 4**, it
 197 is evident that chabazite only forms after 7 days of curing in formulations with: (*Si:Al* = 2.0, *Na:Al* = 1.28),
 198 (*Si:Al* = 1.57, *Na:Al* = 0.91), and (*Si:Al* = 2.0, *Na:Al* = 1.38). These formulations have *Ms* values of 1.19,
 199 1.26, and 1.62, respectively. It is well known that a $Ms > 1.0$ promotes the formation of silica oligomers
 200 (*e.g.*, bridged cyclic tetramers, cyclic trimers, and linear trimers), which would yield better interaction with
 201 TMAAOH, as previously explained [39,40]. Besides interacting with the initial activating solution, the
 202 TMAAOH, with a lower ratio of charge per molecule size compared to Na^+ , more likely stabilizes higher
 203 *Si:Al* aluminosilicates that possess a lower number of balancing negative charges [53]. During alkali-

204 activation, nucleation of these zeolites results from precipitated aluminosilicate gels similar to the ‘gel 2’
205 described in [54] (Si:Al ~2.0).

206 In contrast, the use of activating solutions with Ms lower than unity ($M_s = 0.63$) yields the
207 formation of low Si:Al zeolites as verified by the formation of sodalite in formulations with (Si:Al = 2.0,
208 Na:Al = 1.74). In these low- M_s activating solutions, the majority of silica species are monomers with
209 remnant dimers and trimers [38–40,55]. These species are highly reactive and favor the rapid formation of
210 low-Si:Al gels termed “gel 1” [39,54]. Moreover, the formation of sodalite zeolites may also be due to an
211 out-competition of Na^+ over the TMAA^+ cations for sorption surface sites on precursor particles, as seen in
212 a similar system with combined organic-inorganic cations [56]. XRD data confirm TMAAOH’s utility in
213 inducing early-age mineralization in AAMs [57,58].

214

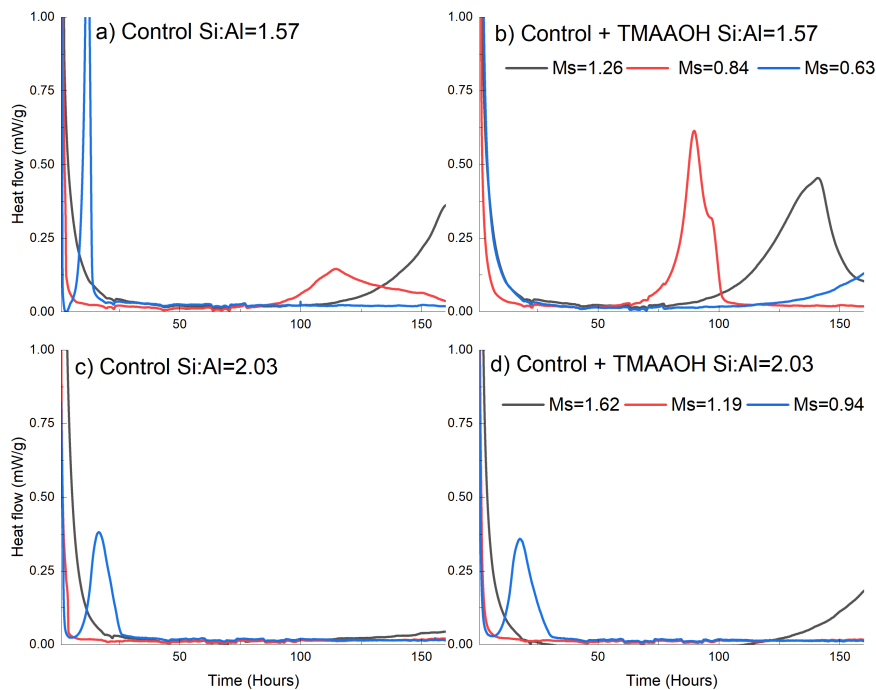


215

216 **Figure 4.** X-Ray diffractograms of alkali-activated MK with Si:Al=2.0 at three (72 hours) and seven days
217 (168 hours). C=chabazite ($Si:Al = 2.1$, PDF 00-019-1178), F=faujasite ($Si:Al = 2.3$, PDF 00-012-0228), S
218 = Sodalite Octahydrate ($Si:Al = 1.0$).

219 3.3 Effect of TMAAOH on Reaction Kinetics

220 **Figure 5** shows the heat evolution of the MK pastes without and with TMAAOH addition. The exothermic
221 peaks exhibited in this figure correlate with mineral formation (see **Figure 3** and **Figure 4**) and provide
222 direct evidence of mineralization thermodynamics occurring in these samples. For example, ($Si:Al = 1.57$,
223 $Na:Al = 0.91$) formulations with TMAAOH and $Ms = 1.26$ exhibit higher heat evolution during alkali
224 activation (100.7 J/g) and reach peak heat at earlier timepoints (~30 hours earlier). These results correlate
225 well with XRD, which substantiate that TMAAOH addition in these samples increases the degree of
226 mineralization (content of minerals) by forming silicon-rich zeolites, such as faujasite and chabazite.



227
228 **Figure 5.** Normalized heat flow curves of alkali-activated MK paste formulations with Si:Al=1.57 and
229 Si:Al=2.03, as indicated within the figure (168 hours).

230

231 As observed in **Figure 5b**, formulations with TMAOOH at Si:Al=1.57 and increasing Na:Al ratios
 232 resulted in rapid early-age mineralization. For example, control samples (**Figure 5a**) with a Na:Al=1.84
 233 displayed two exothermic peaks before 3 days, which correlated with faujasite formation in the first 10
 234 hours as observed *via* XRD. Alternatively, samples with TMAOOH exhibit one initial peak and the
 235 formation of both faujasite and sodalite (**Figure 3**). Hence, only in the presence of TMAAOH and a low
 236 Ms, zeolite nucleation is accelerated and occurs in the first few hours upon activation. This finding is
 237 consistent with the *in situ* crystallization mechanisms of ‘gel 1’ explained earlier. While the formation of
 238 low Si:Al ‘gel 1’ proceeds rapidly [59,60], evidence obtained herein indicated that TMAAOH further
 239 accelerated this process *via* zeolitization in this sample. Similar TMAAOH-induced acceleration was
 240 observed for formulations of the same silica content and lower Na:Al ratios.

241 Samples with a Si:Al=2.03 (**Figure 5c** and **Figure 5d**) exhibited similar behavior regardless of
 242 TMAAOH addition. Further analysis of the total heat released from these samples is summarized in **Table**
 243 **2**. The results indicate that a slight increase (8%) in total heat at 7 days is observed for formulations with
 244 TMAAOH and activating solutions with Ms values near unity (Si:Al =2.0, Na:Al = 2.2). An increase in
 245 total heat, as discussed previously, indicates a larger extent of mineral (*i.e.*, faujasite) formation.
 246 Contrastingly, formulations with the same silica content and TMAAOH but activated with solutions of
 247 higher Ms yield up to 35% lower heat of reaction. Reductions in the heat flow produced during alkali
 248 activation and curing are beneficial in regard to reduced thermal shrinkage.

249

250 **Table 2.** Total heat flow from isothermal calorimetry data for all AAM formulations.

Ms	0.63		0.84		0.94	
Na/Al	1.84		1.37		2.2	
Si/Al	1.57		1.57		2.03	
Sample	Control	TMAAOH	Control	TMAAOH	Control	TMAAOH
Heat (J/g): 3 days	109.6	67.5	89.3	84.3	73.6	81
Heat (J/g): 7 days	116.6	80.5	111.7	117.6	79	85.7
Ms	1.19		1.26		1.62	

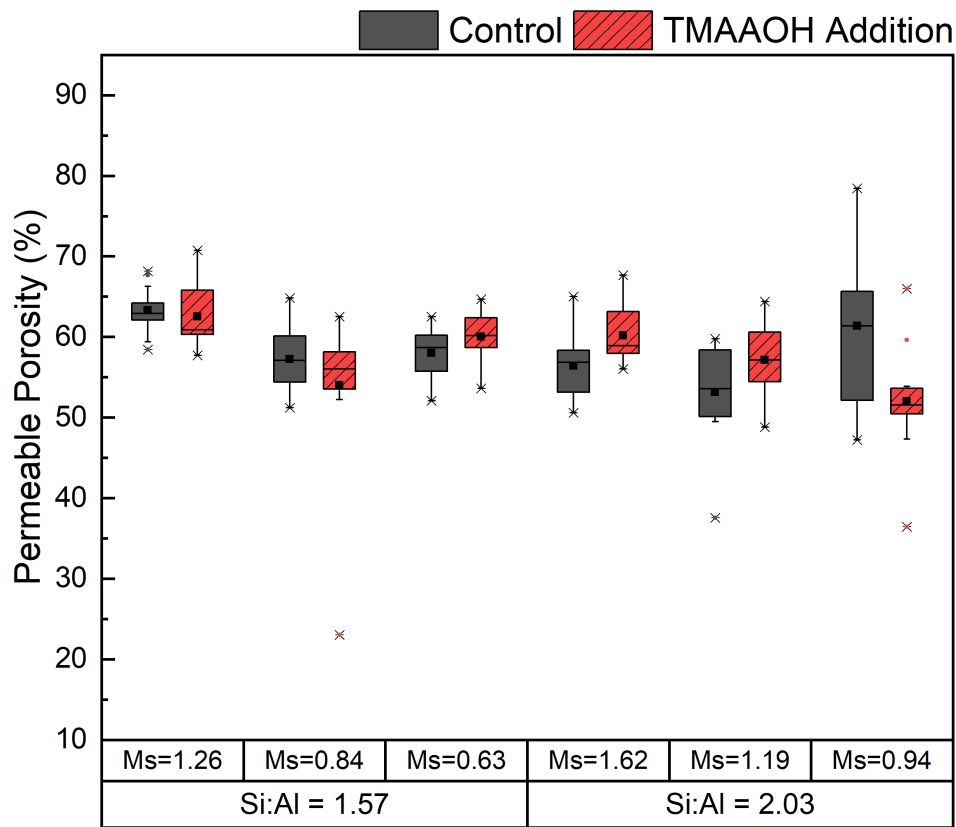
Na/Al	1.74		0.91		1.28	
Si/Al	2.03		1.57		2.03	
Sample	Control	TMAAOH	Control	TMAAOH	Control	TMAAOH
Heat (J/g): 3 days	75.1	74.2	54.9	47	81.3	45.9
Heat (J/g): 7 days	80	78.7	83.6	100.7	88.7	56.5

251

252 **3.4 Effect of TMAAOH on Permeable Porosity and Plastic Shrinkage**

253 The permeable porosities of samples without and with TMAAOH are shown in **Figure 6**. As previously
254 discussed, formulations with $M_s > 1.0$, TMAAOH induced the formation of chabazite, a metastable phase
255 (see **Figure 3** and **Figure 4**). As expected from the authors' previous work [13], the formation of this
256 metastable phase leads to an average increase in the permeable porosity (see **Figure 6**). For example,
257 formulations $M_s=1.62$ and $M_s=1.19$ form chabazite and exhibit an increase in mean permeable porosity
258 of 10% at 7 days. Interestingly, chabazite in $M_s=1.26$ samples do not reveal significant changes in mean
259 permeable porosity, but a larger data variance is observed. In addition, $M_s=0.63$ samples, which were
260 activated with the lowest M_s activating solution, demonstrated rapid mineral formation (**Figure 5**), which
261 led to an an increase (7%) in the mean permeable porosity after seven days of curing.

262



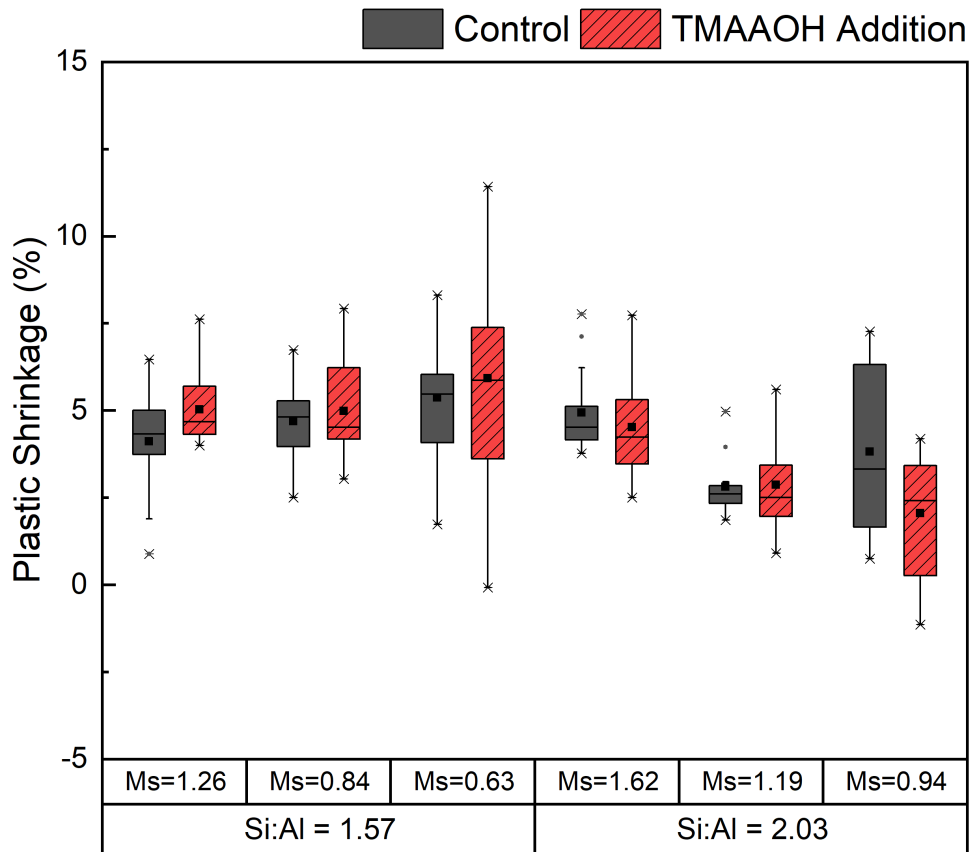
263 **Figure 6.** Permeable porosity of MK pastes without and with TMAAOH addition after 7 days of curing, n
 264 = 9.
 265

266 AAMs activated with TMAAOH and Ms near unity demonstrate an equal or lower permeable porosity as
 267 those without TMAAOH (**Figure 6**). This lower permeable porosity is attributable to a greater extent of
 268 faujasite formation. Early-age faujasite mineralization was confirmed *via* XRD (**Figure 3** and **Figure 4**)
 269 and evidenced in calorimetry measurements (**Figure 5** and **Table 2**). More specifically, TMAAOH addition
 270 reduced the mean permeable porosity in mixtures with Ms=0.84 and in mixtures with Ms = 0.94) 1% and
 271 16%, respectively (see **Figure 6**). As explained by the authors in [13] and further confirmed by [19], the
 272 controlled growth of a silicon-rich zeolite (*i.e.*, faujasite) lowers the permeable porosity in low-calcium
 273 AAMs. Interestingly, these reductions in permeable porosity seem to be unrelated to the framework density
 274 of the zeolites formed. Although chabazite (15.1T/1000A) and sodalite (16.7T/1000A) have greater
 275 framework densities than faujasite (13.3T/1000A) and are thereby less porous, the mixes in which these

276 zeolites developed exhibit a greater permeable porosity than those where exclusively faujasite formed. This
277 perhaps indicates that the time at which the zeolites develop has a greater influence on permeable porosity
278 than the type of zeolite formed. These results provide a limited picture of the effect of TMAAOH on the
279 porosity and microstructure of the alkali activated metakaolin. The high water content of the samples and
280 the tests inability to assess the mesoporosity of the formed zeolites indicate that further testing should be
281 performed to observe changes in other meaningful properties such as the pore size distribution. The results
282 of the permeable porosity should serve as a proxy measurement to initially assess some of the potential
283 microstructural changes.

284 **Figure 7** shows the plastic shrinkage measurements of all pastes. In line with permeable porosity
285 results, the plastic shrinkage of AAMs is lowered when TMAAOH is included as a chemical admixture
286 with activating solutions with a Ms ~1.0. In samples without TMAAOH, there is an expected increase in
287 shrinkage with increases in both Na:Al and Si:Al ratios [61]. Different shrinkage mechanisms apply to
288 TMAAOH-supplemented samples. When TMAAOH is added to AAM mixtures, the rapid nucleation of
289 some stable zeolites (*e.g.*, sodalite) and metastable phases (*i.e.*, chabazite) can result in the formation of
290 silicon-rich N-A-S-H binders susceptible to shrinkage [13]. As previously noted, these mineral dynamics
291 are a result of Ms > 1.0 in the activating solutions. At Ms ~1.0, plastic shrinkage is decreased by 20%, due
292 to a stable increase of faujasite forming in these samples, as evidenced by XRD and isothermal calorimetry.
293 These rudimentary measurements of both permeable porosity and plastic shrinkage provide an initial picture
294 of the impact TMAAOH has on the hardened state properties of these AAM mixtures. However, further
295 studies should be conducted to elucidate the impact TMAAOH (or other SDAs) have on the various types
296 of shrinkage experienced by these materials (*e.g.* drying shrinkage). Taken together, these results illustrate
297 the potencial efficacy of using TMAAOH in combination with activating solutions with Ms ~1.0 to achieve
298 a denser microstructure and lower permeable porosity.

299



300

301 **Figure 7.** Plastic shrinkage of alkali-activated MK paste formulations without and with TMAAOH
 302 addition after 7 days of curing (n = 9).

303

304 **4. Significance and Future Research**

305 By merging the fields of artificial zeolite synthesis with AAMs, this proof of concept work demonstrates
 306 that organic templating agents can be used to manipulate reaction kinetics, early-age microstructural
 307 development, and both fresh- and hardened-state properties of AAMs. Incorporating templating agents as
 308 novel AAM admixtures could increase their tailorability and lead to performance improvements. For
 309 example, the controlled development of early-age faujasite in this study could lead to beneficial
 310 mineralogical and microstructural changes. We showed that, when templating agents are utilized in
 311 activating solutions with a Ms near unity, the early-age formation of faujasite can reduce the volume of

312 permeable pores – a critical factor that reduces chloride diffusivity and, in general, improves long-term
313 durability [13]. Moreover, it is suspected that faujasite and chabazite themselves have the potential to affect
314 chloride transport by increasing chloride binding [62], which could lead to increased chloride binding
315 within these microstructures. Beyond the zeolites templated in this study, other zeolites like 13X FAU, a
316 well-known CO₂ sorbent [63], could be templated to increase CO₂ capture in geopolymer pastes. The
317 potential for process-structure-property exploration into how various templating agents and their
318 chemistries interact with geopolymerization to mineralize the desired zeolites provides a fruitful new area
319 of research related to *mineralization* or *zeolitization admixture* technology.

320 Furthermore, the work herein demonstrated that templating agents could be developed into a new
321 class of *viscosity-modifying admixtures* for geopolymer pastes. Our results show that the incorporation of
322 TMAAOH increased yield stresses of MK geopolymer pastes regardless of Si:Al or Na:Al ratio. Future
323 research is needed, however, to test a suite of chemically tailored viscosity modifying admixtures, which
324 could be developed using one or more various templating agents in combination. Developing various
325 viscosity-modifying admixtures would widen the range of AAM applications, especially those involving
326 additive manufacturing in 3D concrete printing.

327 It is important to note that this work has some inherent limitations. A limited number of mixes
328 were explored, all with high liquid to solids ratios, which generally led to high porosities. Additional
329 research would be needed to design and optimize mixtures with SDAs for specific applications to achieve
330 target physical and mechanical properties and acceptable durability performance.

331

332 **5.0 Conclusion**

333 In this study, we demonstrated that TMAAOH could be utilized as a new chemical admixture in AAMs to
334 induce the early-age formation of silicon-rich zeolites. TMAAOH is observed to directly affect the
335 polycondensation of silica species during alkali-activation, which manifested as quantifiable increases in
336 yield stress and plastic viscosity of the mixtures. Such increases were observed to be much higher for

337 mixtures activated with silica moduli near unity ($M_s \sim 1.0$). This observation indicates that TMAAOH will
338 preferentially interface with short-chained silica oligomer species.

339 The enhanced formation of faujasite *via* TMAAOH templating is attributable to its capability of
340 nucleating a high Si:Al framework. The results suggest that TMAAOH follows a direct *in situ*
341 crystallization methodology, which favors the precipitation of aluminosilicate gels and consequent zeolite
342 nucleation. When TMAAOH was utilized with M_s above unity ($M_s > 1.0$), samples were observed to form
343 faujasite and chabazite (**Figure 2** and **Figure 3**), two well-known silicon-rich zeolites. The formation of
344 chabazite, a metastable zeolite, led to increases in permeable porosity and plastic shrinkage. Contrastingly,
345 the controlled formation of faujasite with activating solutions having a $M_s \sim 1.0$ and TMAAOH resulted in
346 reduced permeable porosity and plastic shrinkage. Lastly, the total heat of reaction for samples including
347 TMAAOH was lower than their control formulations.

348 The results presented herein indicate the need for further investigation into the potential for
349 structure-directing agents to serve as potential mineralization or zeolitization admixtures to tailor the fresh-
350 and hardened-state properties of AAMs. Furthermore, this study highlights the possibility of investigating
351 other templating agents for material-modifying properties, as well as an ability to induce the formation of
352 useful zeolites. For example, this new class of chemical admixtures could promote the formation of
353 functional zeolites in AACs that further densify the microstructure, increase chloride binding, reduce
354 chloride transport, and enhance *in situ* CO₂ sequestration.

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